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PRIMARY OR SECONDARY ELECTROCHEMICAL GENERATOR

FIELD OF THE INVENTION

The invention relates to a high power density primary or secondary generator and, more specifically a generator in which at least one electrode is composed of a solid material characterized by a mesoscopic morphology. An electrolyte is present in the mesoporous network of said electrode forming a bicontinuous junction of very large surface area with the electroactive solid.

The invention also relates to an electrode of this type having a large ion exchange capacity and high electric power density that makes it particularly suited for application as a cathode or anode in a primary or secondary electrochemical generator, such as a lithium ion battery.

The invention also relates to processes for obtaining an electrode of this type involving sol gel precipitation and subsequent baking of the electrically active solid material. It discloses methods to produce the specific mesoporous morphology of the electrode, required for optimal performance of the electrochemical generator. More specifically, it discloses the use of surfactant assemblies as templates to induce the desired electrode texture during the formation of the electro-active solid.

To enhance the performance of the electrochemical generator, in particular with respect to its energy density and power density, all its constituent elements, in particular the electrode materials, the current collector, as well as the separator and the composition of the electrolyte have been scrutinized to allow for the judicious selection of the optimal combination of said constituents. The physical configuration of the generator elements, notably the effect of electrode and spacer thickness and porosity as well as their conformation has been examined.

DESCRIPTION OF PRIOR ART

European patent application EP 0 709 906 A1 discloses a positive electrode composed of a sintered mass of lithium compound oxide, the mean particle size of the electrically active powder being 33 µm. The particles are pressed into pellets of 1.5 mm size by applying high pressure with simultaneous baking at 350 to 700 °C. They report an improvement in the resistivity when baking at the elevated temperature presumably due to a degree of sintering within the active mass, thus improving somewhat the connectivity in the active material. U.S. Pat. No. 5,604,057 discloses a cathode comprising amorphous microporous, sub-micron-size, lithium intercalateable manganese oxide having an internal surface area greater than about 100 m^2/g. Electrodes are fabricated by mixing the oxide with a binder, containing optionally a conducting polymer and heating the composite material at a temperature up to 400 °C. The temperature is limited to this value to prevent crystallization of manganese oxide. The high surface area and the amorphous nature of the active material structure proposed seem to increase the initial capacity of fabricated electrodes but the connectivity is hindered. Interior connectivity of the particles is poor and therefore requires a binder and/or a conducting binder within the electrode fabrication mixture. Another drawback in electrode construction with the amorphous material is that the exposure to temperatures can alter its structure by crystallization, limiting the reported benefits arising from its amorphous structure.

U.S. Pat.No. 5,211,933 and 5,674,644 disclose a method for the low temperature preparation of the spinel $LiMn_2O_4$ and layered $LiCoO_2$ phases prepared at temperatures less than 400 °C using acetate precursors. The $LiMn_2O_4$ powder obtained comprises grains or crystallites ranging in size between 0.3 µm and 1 µm. Pellets are pressed containing this powder and about 10% carbon black and used as positive electrodes in lithium ion batteries. The particle sizes claimed are large to suit high rate discharge electrodes and connectivity within the active material particles is not ensured by special bonding, the conductivity enhanced by mixing in carbon powder to the active powder.

U.S. Pat. No. 5,700,442 discloses insertion compounds based on manganese oxide usable as positive electrode active material in a lithium battery, prepared by reacting β-MnO_2 powder with a lithium compound at 150 to 500 °C for an adequate time to convert these solid precursors to a spinel type. The specific surface of the resulting powder is below 7 m^2/g. The large particle sizes, as deduced from the low specific surface area claimed here are not suited for high rate discharge electrodes.

European patent application EP 0 814 524 A1 discloses a spinel-type lithium manganese complex oxide for a cathode active material of a lithium ion secondary battery. The average particle diameter is between 1 and 5 µm and the specific surface area between 2 and 10 m^2/g. The large particle sizes, thus the low specific surface areas claimed here, are not optimum for high rate discharge electrodes.

BRIEF SUMMARY OF THE INVENTION

As compared to these known features of the prior art, the invention provides and electrochemical generator in which at least one electrode consists of a mesoscopic, bicontinuous structure, composed of an interconnected solid material and of an interconnected network of mesopores. The electrically active solid is employed as a host for accommodating ions by an insertion process. At the same time, it serves to sustain the flow of electric current during charging

and discharging of the battery. Said electrically active solid is in contact with an interconnected porous space filled with electrolyte, the latter serving for ionic transport. Said electrode is characterized by the presence of an extremely large interface between the solid and the electrolyte, comprised between 10 and 3000 m^2/g electrode material, permitting rapid exchange of ions between the solid and liquid phase. The architecture of the solid phase is designed to overcome the impediment of ionic diffusion in the electrolyte encountered with conventional high surface area electrodes. The specific three dimensional structure of the electrode disclosed by the invention ascertains interconnectivity and mechanical stability of the solid phase providing ease of access of the electrolyte to the entire pore space. Furthermore, it renders possible the conduction of electric current within the solid even in the absence of conductive binders which are mixed with the electrically active material in conventional batteries to enhance electronic conductivity of the electrode. The electrically active material in the form of such a mesoscopic morphology is obtained, for example, by employing surfactant assemblies exerting a templating effect during the formation of the solid from water-soluble precursor compounds or by sol-gel synthesis of a xerogel and subsequent sintering under appropriate conditions.

BRIEF DESCRIPTION OF THE INVENTION

Electrodes of lithium manganate, $LiMn_2O_4$ serving as cathode in the electrochemical generator are prepared by casting an aqueous mixture of the manganate precursor by the doctor blading technique or by screen printing or dip coating of the substrate. The gel precursor is precipitated starting from homogeneous solutions of maganous diacetate or manganous diacetylacetonate at 0.13 M and LiOH at 1.3 M. The [Li]/[Mn^{3+}] ratio equals to 10 for each precipitation reaction. The reaction temperature is fixed at 110°C and the pH of the reactants is increased to basic values (~12-13) using the concentrated LiOH solution. In each experiment, the manganous salt solution and the LiOH solution are separately dissolved, before mixing them in a batch reactor with agitation. The reaction time is 2 hours after which the hydrolytic

reaction between LiOH and the manganate salt is terminated by rapidly cooling the solution to less than 10°C in an ice bath.

The gel it is applied in concentrated form to the substrate. Its consistency is controlled by the proportion of water in the mixture and the effectiveness of ambient drying of the cast layer. Each layer provides 0-3 μm (microns) of the dry precursor in porous form. This process is repeated to build up layers of many μm (microns). After deposition of the precursor, the film is heated at 700-750 ^{o}C in air with a temperature gradient of 5-10 ^{o}C/min. and few minutes rest at peak temperature. Figure 2 present the morphology of the electrode obtained by scanning electron microscopy.

An electrode of this type having in its composition an electroactive material in the form of a mesoscopic morphology provides a high energy storage capacity and high power density and may be used in both primary and secondary electrochemical generators. The electrolyte used in such a generator is preferably one containing protons or lithium ions. Other alkali or alkaline earth metals may also be used. According to a preferred embodiment, the electrolyte contains lithium ions brought into the form of one of its salts such as tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate, hexafluoroarsenate, trifluoromethane sulfonate, bis (trifluorosulfonyl) imide, tris (trifluorosulfonyl) methide, trifluoromethanesulfonate, trifluoroacetate, tertachloroaluminate or perfluorobutane sulfonate. According to the preferred embodiment, the solvent of the electrolyte is an aprotic solvent or a liquid salt, such as ethlyene carbonate, propylene carbonate, dimethylcarbonate diethylcarbonate, dioxolane, butyrolactone, methoxypropionitrile, methoxy-ethoxy propionitrile, methoxy-diethoxypropionitrile, methoxyacetonitrile, tetrafluoro-propanol or mixtures of these solvents. Another preferred embodiment of the invention uses a molten salt as a solvent for the lithium ion containing salt, such as methyl-ethyl-imidazolium trifluoromethansulfonate or methy-ethyl-imidazolium bis (trifluorosulfonyl) imide and corresponding di-methyl-ethyl-imidazolium salts with the above anions. The material used for at least one electrode in form of a mesoporous layer may be an electrically active material, but according to the preferred embodiment, this material is chosen so as to form an insertion compound with alkali or alkaline earth metals, thereby

providing a secondary electrochemical generator. An electrically active material of this type will be chosen for example from the oxides or chalcogenides of transition metals or their lithiated or partially lithiated forms, such as TiO_2, Nb_2O_5, WO_3, MoO_3, MnO_2, $Li_yMn_2O_4$, HfO_2, TiS_2, WS_2, $TiSe_2$, Li_yNiO_2,Li_yCoO2, $Li_y(NiCo)O2$, or Sn_yO2. According to the preferred embodiment of the invention, an electrode, which may be the cathode or the anode, depending on the electrical activity of the electrode used as the counterelectrode, is composed of mesoporous titanium dioxide in the form of anatase or in the form of a mixture of rutile and anatase, containing more than 50% anatase. In the presence of lithium ions, the titanium dioxide in mesoporous form is prone to form an intercalation compound Li_yTiO_2 in which the intercalation coefficient has a high value between 0.6 and 0.8. For a cell in which x = 0.8 and where the counterelectrode is made of lithium metal, the theoretical energy density is 400 Wh kg^{-1} assuming a mean value of the cell voltage of 1.5 V. This high capacity is associated with a high value for the specific power , the later reaching values of 2.3 kW/kg. Results of this kind can not be obtained with the technologies of the prior art, such as described by W.J. Macklin et al. (Solid state Ionics 53 -56 (1992) 694-700) in which both the specific power and capacity of a conventional TiO_2 electrode is significantly lower.

When an electrically active compound also capable of inserting lithium ions is used for the other electrode, the electrochemical generator of the invention is a secondary (rechargeable) generator of the “rocking chair” type, the principles of which was descibed for the first time by M. Armand (Materials for Advanced Batteries, D.W. Murph et al. ed. Plenum press N.Y. 1980, p145). According to a preferred embodiment of the invention, the rocking chair configuration employs TiO_2 in the anatase structure as anode material, while $Li_yMn_2O_4$ in amorphous or crystalline form is used for the cathode. The $Li_yMn_2O_4$ ($y \leq 2$) material disclosed by the invention is also present in the form of a mesoporous morphology, yielding cathodes of high capacity, i.e. close to the theoretical maximum of 280 Ah kg^{-1}. The overall capacity of such a $TiO_2/Li_yMn_2O_4$ rocking chair battery reaches up to 140 Ah kg^{-1}, the average cell voltage being

2 volts and the power density based on the material densities 2000 to 3000 W/kg. For such a $TiO_2/Li_yMn_2O_4$ rocking chair thin layer cell configuration power densities of 0.5 to 1.5 mW cm^{-2} μm^{-1} are observed.
The mesoporous electrode structure of the said cell configuration and the battery device as a whole also provide for improved local heat dissipation or exchange from the solid during high rate discharge, thus protecting potentially sensitive (active) materials of the battery from degradation, as exposure to extreme temperatures is minimized.
The mechanical strength is enhanced by controlled sintering process, as the interconnected loops and/or arches are created having a typical aspect ratio of ca. 4, complementing the contribution to the reduction of the system entropy resulting from the natural self-organizing by the templating effect, leading to a structural toughness and robustness of the mesoporous network that can therefore sustain the capillary forces, i.e. not breaking under the intense local pressure when the pores are filled with electrolyte, and most importantly, able to support the strain and mechanical stresses resulting from the volumetric expansion/contraction resulting from the Li^+ insertion/extraction process during the rocking chair battery operation. The later effect induces improved structural integrity on cell cycling, which produces enhanced cyclability as capacity fading due to active material disintegration and discontinuity (decreased electrical connectivity and conductivity) is minimized. Consequently, better solid phase connectivity is ensured with the above mentioned smaller sized "particles" or "grains" or described elemental structural units comprising the mesoporous electrode.
The preparation according to the preferred embodiment of the invention, results in a crystalline phase that enhances the Li^+ insertion kinetics as long crystalline rows are formed at high temperatures and at short times. The sintered metal oxide layer density (and pore or future anhydrous electrolyte mass vs. oxide mass ratio) can be controlled by solvent (e.g. water) dilution of the oxide precursor and the aggregation state (oxide mass vs. water) of the precursor solution applied.

The full connectivity of the mesoporous space combined with the low tortuosity enables a lower porosity (higher active mass to void (for electrolyte) ratio) to be more effective with respect to the electrolyte function i.e. Li^+ diffusivity.
The two proposed mineral electrodes instead of carbon or lithium metal offer safety in a battery device as the risk of explosion is virtually eliminated in the former case. The battery concept, as of the preferred embodiment of the invention described above, embodies the safety aspect by considering only non-water sensitive and low toxicity materials for electrode fabrication and for the electrolytes as well. Carbon electrode surfaces are very reactive and especially so at high current rates, and require overcharge protection. Also nickel-cobalt oxides are prone to dangerous reactions as well. The manganese oxides are safe in all respects and no charge protection is necessary.

BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the invention are further set out in the following examples, given by way of non-limiting example with reference to the appended drawings in which:

FIG.1 shows a side view of an electrochemical generator of the invention with a partial sector showing the arrangement of the internal layers; (1,2) active material mesoporous electrode layers, (3) the porous separator layer, (4,5) the current collectors.
FIG.2 shows SEM images of the said mesoporous lithium manganate sintered layer under time and conditions set according to a preferred embodiment of the invention.
FIG.3 shows cyclic voltammograms of 1.5 µm layers of the said lithium manganate as a function of treatment temperature.
FIG.4 shows the comparison under shallow cycling of the various types of electrodes under identical potential scan and electrolyte conditions, in order to demonstrate the improved kinetics in the charge/discharge performance of said mesoporous lithium manganate material as a positive electrode.

FIG.5 shows the electrolyte function at steady-state current of the thin layer battery as perceived by the simulation model describing the electrolyte transport behavior of a completely mesoporous cell, by means of the concentration profiles of the Li^+ and the coupling anion species within a multilayer design.
FIG.6 shows examples of electrolytes and their electrochemical properties used in the cell described above.
FIG.7 shows examples of several differently sized $TiO_2/Li_yMn_2O_4$ accumulators with respect to current and voltage discharge behavior. All cells utilize pure cellulose paper (30-40 µm (microns)) as the separator.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE 1

According to a first embodiment, a secondary electrochemical generator of the "rocking chair" type has $TiO_2/Li_yMn_2O_4$ negative and positive electrodes respectively and of the cell configuration depicted in Figure 1. The mesoporous layers are deposited on conducting tin oxide coated glass sheets by the methods previously described. Devices display 20C (or C/0.05) discharge rates under short circuit. The above cell in 30 cm^2 form battery and a thin layer configuration comprising 10 µm (micron) mesoporous layers of the active materials, according to a preferred embodiment, with a separator of pure cellulose paper of 30-40 µm (microns), utilizing electrolyte comprised of methoxypropionitrile and lithium bis-(trifluorosulfonyl) imide, is observed to sustain a 10C (or C/0.1) discharge rate and maintain a cell voltage of 1.5V, resulting in power densities above 1500 W/kg and energy densities above 210 Wh/kg.

EXAMPLE 2

The porosity of a typical sintered layer of the nanosized oxide of an average 8µm layer estimated by mass to surface measurements reaches as high as 30-70%. Very porous appear to be the layers in the case of 1.5 µm (micron) sintered films treated at 400 and 700 ^{o}C, the behavior of which is seen in

Figure 3. The two insertion levels for the spinel in the 4V range reported in the literature (W. Liu et al., J. Electrochem. Soc., Vol.143, No. 3, (1996), 879-884) for 200nm layers at 0.05mV/s, appear very distinct for our 1.5 μm (micron) thickness recorded at a sweep rate over two orders of magnitude higher, demonstrating the higher reversibility in the intercalation kinetics in comparison to the earlier materials, attainable by decreasing the particle size to the nanometer range and simultaneously ensuring effective particle connectivity and mesoporosity. The 700^{O}C material appears to be less resistive and increased electrochemical reversibility and the capacity much higher as compared to the 400^{O}C treatment due to the effective interconnectivity by sintering and material formation at the high temperature, as seen in Figure 2.

EXAMPLE 3

Sintering the primary particles in order to obtain a bicontinuous porous network and thus a high connectivity should therefore be determinant to performance. The idea toward improving the manganates by imparting mesoscopic morphology to a continuous phase i.e. by retaining the connectivity as well as decreasing the primary particle to the nanometer range, significant improvements to the intercalation properties are expected. Making intimate electrical contact within the active mass regardless of size and shape of the oxide, results in enhanced utilization of the oxide and is therefore very desirable. For comparison electrodes are made from the commercial spinel $LiMn_2O_4$ materials, namely the Selectipur and 5.2 μm (micron) particle powders, both supplied by Merk. The Selectipur particles consist of large hollow spheres (30 μm (micron)) the walls of which appear on SEM to have primary grains of 100-200 μm (microns), extremely tight merged packing; the other appears as a fragmented form of the Selectipur. The pre-formed powders are made into electrodes by mixing the powder with PVA (MW 100000) as binder and graphite particles (Lonza KS-10 or carbon nanotubes) as the conducting matrix. The weight percentage of the constituents are chosen maximum 3% PVA and 10% graphite. The pastes are cast on CTO substrates ambient dried and then heated in an air furnace for 15min at 200 ^{O}C. As electrolyte a 1M $LiClO_4$ in propylene carbonate is the standard in all electrode cycling

experiments to enable objective comparison. Depicted in Figure 4 is the comparison between the Merck powders and a 8 µm (micron) mesoporous layer under shallow cycling of the various types of electrodes under identical potential scan and electrolyte conditions, in order to demonstrate the improved kinetics in the discharge performance of said mesoporous lithium manganate material as a positive electrode. Cyclic voltammetric information elucidates the kinetic aspects of the lithium insertion/extraction in the oxides of the above thin film electrodes. The Selectipur and 5.2 µm (micron) particle electrodes display higher irreversibility than the electrode from the mesoporous material treated at 700 ^{o}C. as evidenced by the higher induced polarization and discharge peak potential shift toward more negative in the case of the commercial materials. The mesoporous layer shows a clear advantage over the even higher capacity (larger active mass) Selectipur electrode that contains conducting carbon.

EXAMPLE 4

The preferential kinetics are also exemplified by the comparison of the Selectipur 30-40µm electrode the 8µm mesoporous layer. In the same voltammetric set up and under a potential scan of 100mV/s a 1.75 to 2 mA/cm^2 delithiation current at 1.5V vs. AgCl and 7.5 mA/cm^2, in both cases respectively. At 20mV/s a 1.25 mA/cm^2 current was measured in the first case and 5 mA/cm^2 in the second. As another example a 3 µm (micron) $LiMn_2O_4$ electrode in PC, 1M Li^+, at short circuit gave a 1.4 mA/cm^2/ µm (micron) on charge and discharge. The corresponding value for the delithiation of TiO_2 was 0.4 mA/cm^2/ µm (micron). The above Selectipur 30-40µm electrode gave 0.055 mA/cm^2/ µm (micron).

Cyclability was the normally expected for the temperature treatment applied and described in the literature. In the glove box, 10% capacity loss was observed within the first 50 cycles at 5 mV/s scan rate and between 1.4 - 2.8V as voltage limits.

EXAMPLE 5

Thin layer cell ionic transport conditions at steady-state are modeled for the mesoporous electrode intercalation cell. The cell configuration consists of two 1millimeter lithium intercalation mesoporous hosts separated by a 20 μm (micron) inert and insulating (meso-)porous spacer, one of the active material layers acting as the insertion and the other as the de-insertion (lithium extraction) electrode. The initial electrolyte concentration in monovalent lithium salt is 1M and the free stream diffusion coefficient for Li^+ in the electrolyte corresponds to the case of propylene carbonate (3 10^{-6} cm^2/s) of approximately 3 cP.

In the depicted results of the model the concentration profile of the Li^+ (also the overlapping curve for the anion) appears in Figure 5a and the potential drop across the cell in Figure 5b when approx. 6 mA/cm^2 are passing through the cell, the minimum current limiting the supply of Li^+ to one side of the intercalating electrode. The conductivity of the host solid is not considered here. The electrode porosities are 50% and 90% for the separator layer.

Anything smaller than 1000 μm (micron) (1mm) would increase the limiting currents. It is noted that the absence of supporting electrolyte in this case aids the lithium ion diffusion or transport but at a cost of potential in the form of IR drop across the cell (here just under 0.2 V, as depicted in the Figure 5b. This calculation reveals that for electrodes of 10 μm (microns) in the above configuration, currents as high as 500mA/cm^2 are possible as far as electrolyte performance is concerned.

In addition, the TiO_2/cellulose paper/LiyMn2O4 cells, with active mesoporous layers of about 10 μm (microns), could deliver more than 5mA/cm^2 at short circuit, with molten salts containing 1-2 M lithium - bis (trifluorosulfonyl) imide that has a much higher viscosity (>40 cP) than in the propylene carbonate case, and thus a lower Li^+ diffusion coefficient.

EXAMPLE 6

From the viewpoint of electrolyte investigation and characterization the sought for properties are generally low viscosity, low volatility, solubility of the lithium salt electrolytes and electrochemical stability/chemical compatibility with the electrode materials. Synthesized are room temperature ionic liquids which have very attractive features in the above respects. The electrochemical stability limits fulfill the requirements for 4V cathode materials, as seen from the examples shown in Figure 6a. The potentials are expressed versus iodide/tri-iodide which is +0.15V vs. AgCl. Di-methyl-ethyl-imidazolium imide offers the best cathodic stability advantages.

Solubility of more than 2M lithium-bis (trifluorosulfonyl) imide can be reached in methoxy-diethoxy propionitrile and in methoxypropionitrile. The electrochemical stability of this newly synthesized organic solvent as evidenced by the electrochemical window is given in Figure 6b. The corresponding stability range for methoxypropionitrile is depicted by the bar in this figure, and the operation limits of the lithium hosts TiO_2 and lithium manganate are positioned against this scale (ferrocene potential is +0.4V vs. AgCl) in Figure 6c.

These molecular structures are designed to exploit the strong solvating properties of the ether groups toward Li^+, combined with the low viscosity for Li^+ diffusion and the relatively high boiling points of these compounds to decrease their volatility. Methoxy-ethoxy-propionitrile is also synthesized having viscosity 2.7cP, 1.1cP being for methoxypropionitrile and 5cP for methoxy-diethoxy propionitrile. The boiling points are respectively 240C, 165°C and at 10 mmHg 152°C.

EXAMPLE 7

According to a second embodiment, a secondary electrochemical generator of the "rocking chair" type has $TiO_2/Li_yMn_2O_4$ negative and positive electrodes respectively as described in EXAMPLE 1 and of the cell configuration depicted in Figure 1, however, with the separator layer (3) consisting of a mesoporous zirconia layer of 8 μm (micron) thickness and 60% porous, prepared as described

by P.Bonhote et al., J.Phys.Chem.B. (1998), 102, 1498-1507, displays performance characteristics matching those disclosed in EXAMPLE 1. This mesoporous separator offers advantages for electrolyte penetration in the phase of electrolyte filling of the said electrochemical generator and effective retention of the electrolyte within the mesopores and thus within the generator as a whole, combined with effective displacement of gas from the space of the said generator on electrolyte filling, as well as during operation, that is the effective accommodation of volumetric changes on charge/discharge cycling, allowing for electrolyte movement and gas expulsion from the generator layers(1,2,3) by forced capillary filling of the pores by the liquid electrolyte.